

Crystal and Molecular Structures and Experimentally Determined Charge Densities of Fluorinated Ethenes

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Abstract: Crystals of various fluorinated ethenes were grown by in situ crystallization from their melts on a diffractometer, allowing the structures of tetrafluoroethene (C₂F₄), trifluoroethene (C₂HF₃), 1,1-difluoroethene (C₂H₂F₂), (*E*)-1,2-difluoroethene (C₂H₂F₂), and (*Z*)-1,2-difluoroethene (C₂H₂F₂) to be determined by X-ray crystallography. Unexpectedly, the C=C bond lengths show only small variations arising from fluorine substitution. These findings are supported by ab initio calculations at a DFT level of theory and the results of topological analyses of the experimentally determined and theoretically calculated charge densities.

Keywords: charge density · ethenes · fluorinated ethenes · fluorine · solid-state structures · X-ray diffraction

Introduction

Fluorinated alkenes are important starting materials for the industrial synthesis of polymers such as polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), polychlorotrifluoroethylene (PCTFE), and poly(vinylidene difluoride) (PVDF),^[1] and so have been extensively studied.^[2] The first structure determinations of tetrafluoroethene and 1,1-difluoroethene date back to the pioneering gas electron diffraction study by I. L. Karle and J. Karle.^[3] Bauer et al. found that the C=C bond length decreases as fluorines are substituted for hydrogen in ethene in a systematic gas electron-diffraction study,^[4] and the values for 1,1-difluoroethene and trifluoroethene are in good agreement with those of an early microwave study.^[5] However, later gas electron diffraction and microwave data obtained by Mijlhoff et al.

show large discrepancies, especially in the values of the bond lengths of the C=C double bond.^[6–11] The structures of (*Z*)-1,2-difluoroethene^[12] (C=C 1.325 Å) and of (*E*)-1,2-difluoroethene^[13] (C=C 1.316 Å) were determined by microwave spectroscopy and high-resolution IR spectroscopy, respectively.

Furthermore, fluorinated ethenes have been the subjects of several theoretical calculations showing either very strong or negligible effects of the degree of fluorination on the C=C bond length, depending on the level of theory and the basis sets (Table 1).^[14–16]

Solid-state structural information on these compounds based on conventional X-ray crystal structure determination is very limited. Crystallographic data for small, highly fluorinated alkenes are available only for potassium hydrogen difluorofumarate,^[19] potassium hydrogen difluoromaleate,^[19] 1,2-difluorodinitroethene,^[20] perfluorocyclopropene,^[21] trifluorovinyl isocyanide,^[22] trifluorovinyl cyanide,^[22] hexafluoropropene,^[23] 1,1-difluoroallene,^[24] tetrafluoroallene,^[24] 1,1,4,4-tetrafluorobutadiene,^[25] tetrafluorobutatriene,^[25] trifluorobutadiene,^[26] and octafluoro-1,2-dimethylenecyclobutane.^[27]

Experimentally measured charge density determinations exist only for perfluorocyclopropene,^[21] 1,1-difluoroallene,^[24] tetrafluorobutatriene,^[25] and octafluoro-1,2-dimethylenecyclobutane,^[27] including a topological analysis for the last three. Chemical applications of X-ray charge density analysis were reviewed recently by Koritsanszky and Coppens.^[28]

In continuation of our work on fluorination effects on small molecules we report here on a systematic X-ray diffraction study of fluorinated ethenes. This experimental work was supplemented by ab initio calculations.

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Supporting information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author. The Supporting Information includes static deformation density maps, relief plots of the negative Laplacians, isosurface maps of the electrostatic potential and tables of the multipole parameters for the title molecules. Color pictures of the figure used in the publication are also included.

Table 1. Summary of C=C bond lengths in ethenes, obtained by gas electron diffraction, microwave spectroscopy and theoretical methods.

	Experimental			Theoretical			
	Bauer et al. ^[a]	Mijlhoff et al. ^[b]	Dixon et al. ^[c] SCF	Dixon et al. ^[c] CI-SD	MP2-6-31G** ^[d]	MP2-TZ2P ^[d]	MP2-6-311G** ^[d]
CF ₂ =CF ₂	1.311(7)		1.307	1.320	1.326	1.322	1.328
CF ₂ =CHF	1.309(6)	1.341(12)	1.307		1.328	1.323	1.330
(Z)-CHF=CHF	1.331(4)	1.330(11)	1.312	1.329	1.328	1.323	1.331
(E)-CHF=CHF	1.329(4)	1.320(9)	1.311	1.328	1.328	1.323	1.330
1,1-CH ₂ =CF ₂	1.316	1.340(6)	1.307	1.323	1.323	1.318	1.326
CHF=CH ₂	1.333(7)	1.330(18)	1.314	1.330	1.327	1.321	1.329
CH ₂ =CH ₂	Duncan ^[e] 1.3384(10)		1.325	1.342			1.335 ^[f]

[a] Reference [4]. [b] References [6–11]. [c] Reference [14]. [d] Reference [16]. [e] Reference [17]. [f] Reference [18].

Results

The molecular structures of the investigated fluorinated ethenes are shown as ORTEP^[29] diagrams in Figure 1. Tetra-

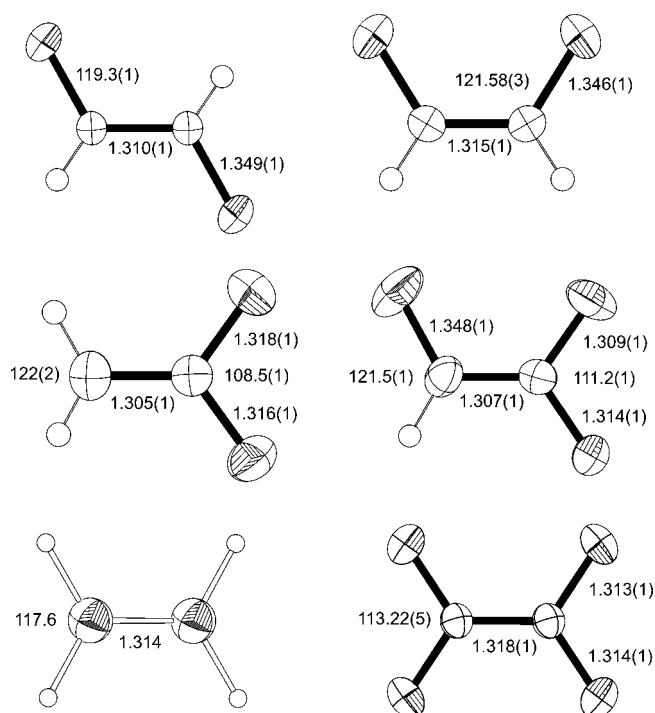


Figure 1. ORTEP^[29] diagrams of the C₂F₄, C₂HF₃, 1,1-C₂H₂F₂, (E)-1,2-C₂H₂F₂ and (Z)-1,2-C₂H₂F₂ molecules in comparison with the data for C₂H₄.^[29] Bond lengths and angles from a spherical refinement (SHELXL), bond lengths from the multipole model agree with the spherical data within 0.005 Å.

fluoroethene crystallizes monoclinic (*P*₂₁/*n*), with half a molecule in the asymmetric unit, creating a molecule with crystallographic point symmetry. The lattice constants and the packing (see Figure 2) are very similar to those of ethene.^[30] Trifluoroethene also crystallizes monoclinic (*P*₂₁/*n*); the unit cell is depicted in Figure 3. The isomeric difluoroethenes form different lattices. (E)-1,2-Difluoroethene crystallizes monoclinic (*P*₂₁/*c*), with one half of the centrosymmetric molecule forming the asymmetric unit, and (Z)-1,2-difluoroethene forms orthorhombic crystals (*Pnma*), again with a half molecule forming the asymmetric unit. The molecule possesses crystallographic C_s symmetry. 1,1-Difluoroethene crystallizes orthorhombic (*P*₂₁2₁2₁) with two molecules

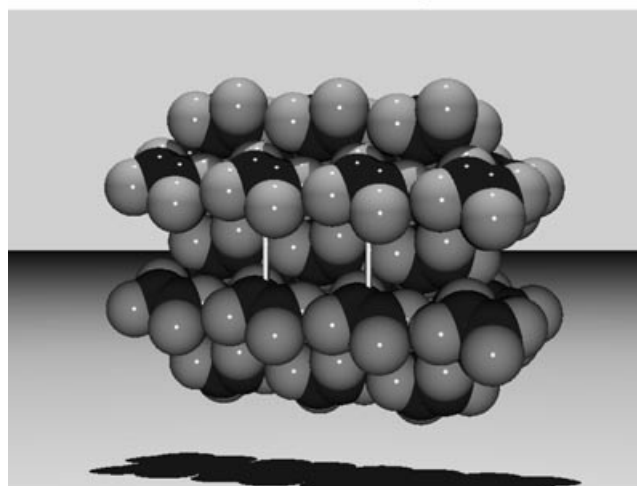
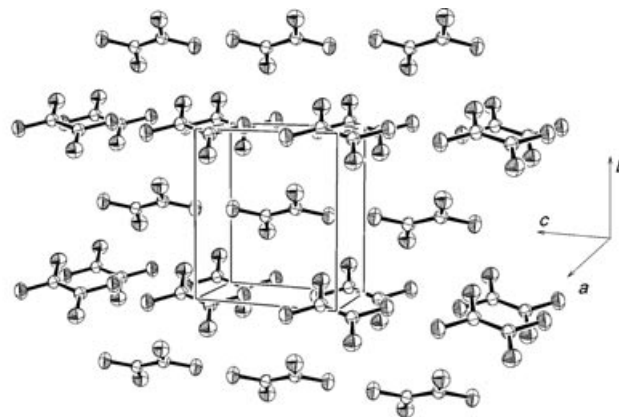


Figure 2. Packing of tetrafluoroethene, ORTEP^[29] (top) and space-filling model (POV-Ray,^[36] bottom).

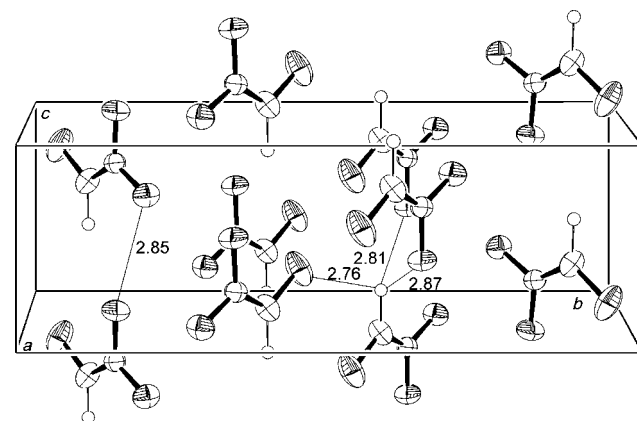


Figure 3. Unit cell of trifluoroethene (ORTEP^[29]).

forming the asymmetric unit, resulting in a rather long crystallographic c axis. A higher symmetric or smaller unit cell was ruled out by use of the PLATON program.^[31] Selected bond lengths and angles are depicted in Figure 1, while the unit cells and packing are presented in Figures 4 and 5, respectively. Analysis of intermolecular distances was performed with the aid of the PLATON^[31] and PARST^[32] programs as implemented in the WINGX^[33] program package.

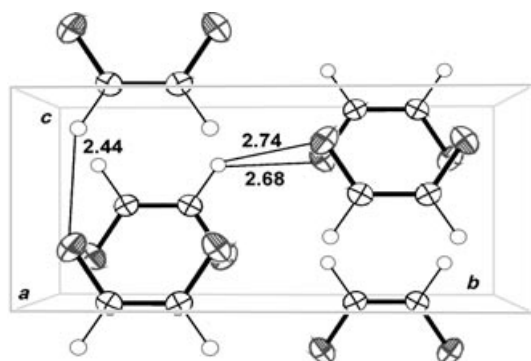


Figure 4. Packing diagram (ORTEP^[29]) of *(Z)*-1,2-difluoroethene (top); view down the a axis. Space-filling model (SCHAKAL^[38]); view along 100 (center) and 0 01 (bottom).

Discussion

Despite the very small estimated standard deviations (esd's) of solid-state X-ray diffraction studies, one has to expect systematically shortened bond lengths due to libration effects, which are difficult to correct for in small planar molecules.^[34] This can easily be demonstrated by the structural data for ethene. An extremely careful X-ray diffraction^[30] study gave an uncorrected C=C distance of 1.3142(3) Å,

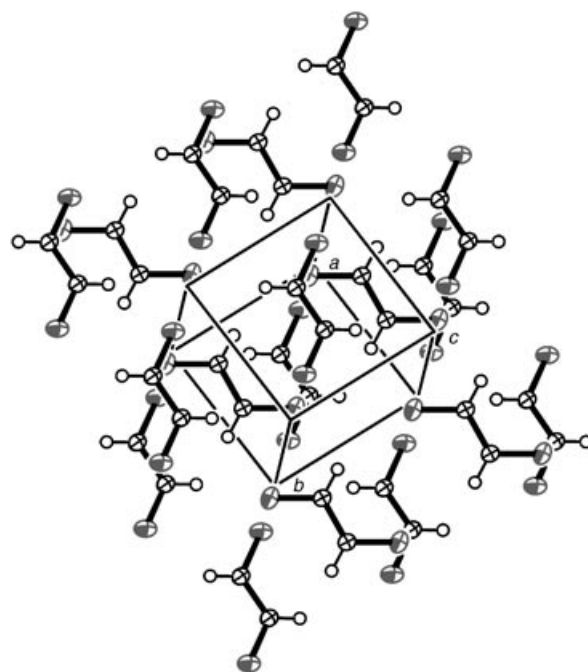


Figure 5. Packing diagram of *(E)*-1,2-difluoroethene (ORTEP^[29] POV-Ray^[36]). View perpendicular to the molecular plane.

whereas very precise gas-phase data resulted in a C=C distance of 1.337(2) Å (Figure 1).^[17]

Although the estimated standard deviations obtained from least squares refinement are very small, systematic errors due to libration effects are at least one order of magnitude larger. Attempts to use the thermal motion analysis program THMA14c^[35] to take account of the libration effects failed for C₂F₄ and both isomers of 1,2-C₂H₂F₂, as the least-squares refinement of the three tensors T , L , and S requires at least 20 independent anisotropic displacement parameters, which cannot be obtained from two or three atoms in the asymmetric units of *(E)*-1,2-difluoroethene, *(Z)*-1,2-difluoroethene and tetrafluoroethene.

Nevertheless, the following conclusions are allowed:

- 1) Differences in C=C bond lengths due to substitution of hydrogen are smaller than 0.02 Å. In contrast with the

results of the electron diffraction study by Bauer et al.^[4] and early theoretical calculations,^[14] the C=C double bond length does not decrease monotonously with the number of fluorine atoms: the smallest C=C bond length is observed in 1,1-difluoroethene. These findings are in close agreement with more recent ab initio results^[15,16] on the MP2 level and our DFT calculations, all of which predict only small effects on the C=C bond length, with the shortest bond calculated for 1,1-difluoroethene.

- 2) Most of the C=C-F bond angles are above 120° and much larger than H-C=C bond angles. This results in small F-C-F bond angles, with the smallest value observed in 1,1-difluoroethene. This fits well with the usual explanation that the fluorine atom prefers orbitals with small s character when forming polar covalent bonds.
- 3) The C-F bond lengths of the CF₂ groups are about 0.03 Å shorter than those of the CHF groups.

Crystal packing: The packing of tetrafluoroethene seems to be influenced by attractive electrostatic interaction between the negative charged fluorine substituents and the positively charged carbon atoms, resulting in a typical herring-bone motive (Figure 2). The shortest intermolecular distances, of 3.11 to 3.15 Å, were found between the fluorine atoms and the carbon atoms.

The same packing was found for ethene, which has exactly the opposite charge distribution.^[30] Nevertheless, no co-crystals were formed in an attempt to co-crystallize a one to one mixture of ethene and tetrafluoroethene. Only tetrafluoroethene—which has the higher melting point—crystallized, as could be seen by comparison of the obtained lattice constants. Interestingly, similar packing is observed for 1,1,4,4-tetrafluorobutatriene.^[25]

The unit cell of trifluoroethene is depicted in Figure 3. All intermolecular distances are equal to or longer than the sums of the van der Waals radii. In particular, all H...F contacts are longer than 2.70 Å. Thus short intermolecular H...F contacts do not seem to play an important role for the lattice energy of this compound. The shortest fluorine contact is in the range of the sum of the van der Waals radii of fluorine.^[37]

The crystal packing of (*Z*)-1,2-difluoroethene is depicted in Figure 4. It is governed by short intermolecular H...F contacts of 2.44 Å, with C-H bond length normalized to 1.080 Å.^[39] This results in chains of individual molecules, oriented along the crystallographic *c* axis. The H...F contacts between these chains are much longer.

The crystal packing of (*E*)-1,2-difluoroethene is shown in Figure 5 in a view perpendicular to the molecular plane. The shortest intermolecular H...F contacts of 2.59 Å of molecules related by the glide plane of (*E*)-1,2-difluoroethene are much longer than those of the *Z* isomer, forming chains of molecules displaying longer H...F contacts between these chains.

1,1-Difluoroethene (Figure 6) crystallizes in the orthorhombic space group *P*2₁2₁2₁, with two molecules forming the asymmetric unit. The two molecules in the asymmetric unit, marked A and B, are arranged in double layers perpen-

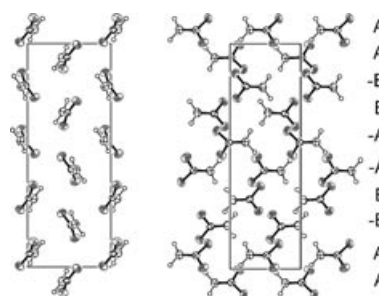


Figure 6. Packing diagram (ORTEP^[29]) of 1,1-difluoroethene. Left view along 100, right view along 010. The two molecules in the asymmetric unit are marked A and B.

dicular to the long crystallographic *c* axis. The individual molecules form columns along the *a* axis in which the partially positively charged hydrogen atoms point towards the partially negatively charged fluorine atoms. The fluorine substituents in the type A molecules of a double layer point in one direction along the positive and negative *a* axis for molecules centered around *z*=0 and *z*=0.5, respectively. Within the double layer of the B molecules, the columns change direction. As can be seen from a view along 100, molecules B form a herring-bone arrangement with themselves and with molecules A, whereas molecules A have almost parallel arrangement. In contrast with the 1,2-substituted isomers there exist no short H...F contacts.

Charge density and topological analysis: The experimentally determined static deformation density (SDD) $\Delta(r)$ was found to be in good agreement with the corresponding theoretically calculated one. As one example, Figure 7 shows the experimental static and the theoretical deformation density maps of (*Z*)-1,2-difluoroethene. Density accumulation is found in the nonpolar bonds (C=C, C-H), in the polar C-F bonds, and in the nonbonded valence shell regions around the fluorine atoms. Both figures show very well that the center of density in the C=C bond is shifted in the direction of the electronegative fluorine atoms. The unexpected greater thermodynamic stability of the *Z* isomer of 1,2-difluoroethene relative to the *E* isomer was attributed to this nonlinear bond path by Wiberg et al.^[40] on the basis of theoretical calculations.

Figure 8 shows the relief plot of the negative Laplacian $-\nabla^2\rho(\mathbf{r})$ of the total density in the molecular plane of (*Z*)-1,2-difluoroethene based on the experimental data. Local valence-shell charge concentrations (VSCCs) in the saddle-shaped regions, as clear indications of the covalent bonds, are seen on the nonpolar C=C bonds as symmetric saddles, while the polar C-F bonds show asymmetric saddles in the relief plots. For the fluorine atoms, maxima of nonbonded VSCCs were also located.

The quantitative results of the experimental and theoretical topological analyses in terms of $\rho(\mathbf{r}_b)$ and $\nabla^2\rho(\mathbf{r}_b)$ values at the bond critical points \mathbf{r}_b are summarized in Table 2. For monofluoroethene only theoretical data were available. Experimentally measured and theoretically calculated bond lengths are in good accordance within 0.008 Å, bond lengths from the multipole refinement differ by no more than

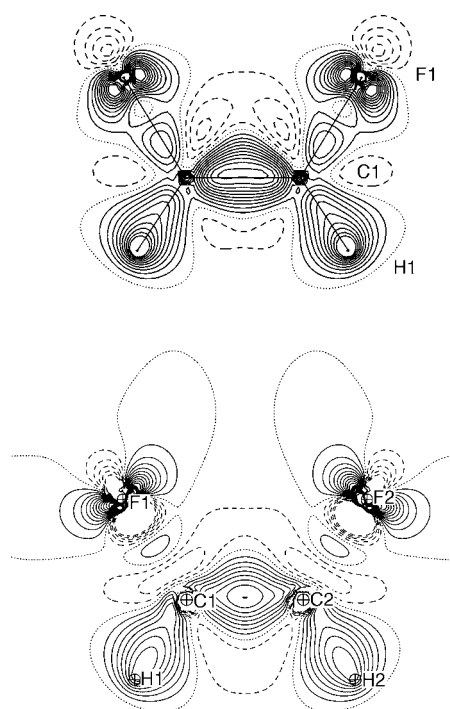


Figure 7. Experimentally determined (top) and theoretically calculated (bottom) static deformation density maps in the molecular plane of (*Z*)-1,2-difluoroethene. The contour intervals are at $0.1 \text{ e} \text{ \AA}^{-3}$, with zero and negative lines dotted and dashed, respectively.

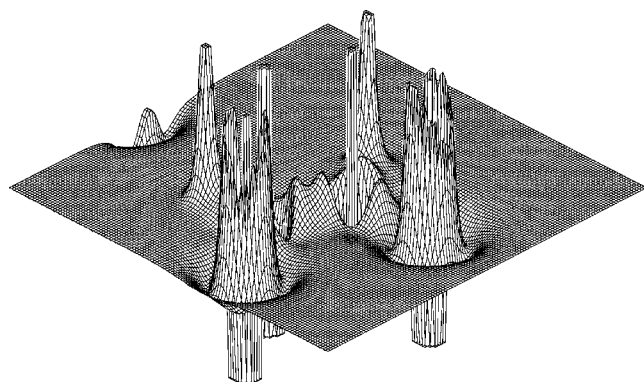


Figure 8. Relief plot giving the negative Laplacian $-\nabla^2\rho(\mathbf{r})$ of the total experimental density in the molecular plane of (*Z*)-1,2-difluoroethene.

0.005 \AA (average 0.002 \AA) from the spherical model. The C–F bonds can be distinguished into two groups: C–F bonds in CFH groups, which are in the $1.344\text{--}1.346 \text{ \AA}$ range, and the shorter C–F bonds in CF₂ groups, in the $1.311\text{--}1.321 \text{ \AA}$ range. The experimentally determined charge density at the bond critical points of the shorter C–F bonds (CF₂) is about $2.16 \text{ e} \text{ \AA}^{-3}$, the theoretical value is about $1.96 \text{ e} \text{ \AA}^{-3}$. The other group of C–F bonds (CFH) has fewer but different experimentally determined values, ranging from $1.85 \text{ e} \text{ \AA}^{-3}$ in (*E*)-1,2-difluoroethene to $2.11 \text{ e} \text{ \AA}^{-3}$ in (*Z*)-1,2-difluoroethene. This is roughly the range for $\rho(\mathbf{r}_b)$ values found in our previous studies on two perfluorinated hydrocarbons.^[25,26] As was also found earlier, the theoretically calculated $\rho(\mathbf{r}_b)$ values for the C–F bonds are smaller than the experimentally ascertained ones by 10–20%.

More significant differences are found between the experimentally determined and the theoretically calculated Laplacians in the polar C–F bonds. The experimentally determined Laplacians at the bond critical points of the C–F bonds range from $-9.6(1)$ to $-23.7(2) \text{ e} \text{ \AA}^{-5}$. In earlier studies, $\nabla^2\rho(\mathbf{r})$ on C(sp²)–F bonds was found to be $-15(4) \text{ e} \text{ \AA}^{-5}$ for *p*-fluoromandelic acid,^[41] $-10.2(4) \text{ e} \text{ \AA}^{-5}$ for 1,1-difluoroallene,^[24] $-18.1(1)$ to $-25.7(1) \text{ e} \text{ \AA}^{-5}$ for pentafluorobenzoic acid,^[42] and $-15(4) \text{ e} \text{ \AA}^{-5}$ for tetrafluorobutatriene.^[25] In all cases the theoretical Laplacian for C–F bonds is close to zero, ranging from -3.00 to $0.50 \text{ e} \text{ \AA}^{-5}$ in the title compounds. In an inspection of the charge density and Laplacian distribution along the polar C–F bond detailed earlier,^[24] it was shown that the theoretical calculations locate the bond critical point $0.05\text{--}0.1 \text{ \AA}$ away from the experimentally determined critical point in a direction closer to the carbon atom. The Laplacian is positive between the nuclei, except for a small range around the VSCC of the carbon atom, and undergoes a change of sign just between the experimentally determined and the theoretically calculated locations. Thus, even a small shift in the critical point location results in significant changes in $\nabla^2\rho(\mathbf{r})$ values. According to Coppens et al.,^[43] the main origin of these discrepancies is attributable to the nature of the radial functions in the multipole model, which contribute to the location of the bond critical points.

One major question of this study was whether the C=C double bond is influenced by the amount of fluorine substitution. It has already been mentioned that no indication of a substitution effect on the C=C bond was found from spherical refinement. This is supported by the multipole model and the topological data. The multipole C=C bond lengths are in the narrow range between 1.308 and 1.318 \AA ; DFT calculations yield 1.315 to 1.321 \AA with no indication of a correlation. The same holds for the bond critical point data: $\rho(\mathbf{r}_b)$ values average to $2.52(10) \text{ e} \text{ \AA}^{-3}/2.46(2) \text{ e} \text{ \AA}^{-3}$ (exptl/theory) showing no trend with respect to the number of fluorine substituents. However, the experimentally determined and theoretically calculated $\rho(\mathbf{r}_b)$ value close to $2.5 \text{ e} \text{ \AA}^{-3}$ is higher than the corresponding quantity in the “standard” C=C bond in ethylene, calculated at the MP2 level as $2.33 \text{ e} \text{ \AA}^{-3}$.^[44]

Conclusion

This study has shown that the amount of fluorine substitution on the ethene molecules does not significantly influence the length or topology of the C=C double bond. However, a difference is seen in the C–F bonds, between the CF₂ and the CHF groups. Both the spherical and the multipole model give C–F bond lengths of the CF₂ groups shorter than for the CHF group by 0.03 \AA .

Experimental Section

Preparation: (*E*)-1,2-Difluoroethene,^[45] (*Z*)-1,2-difluoroethene,^[45] and tetrafluoroethene^[46] were prepared by literature methods. (*E*)-1,2-Di-

Table 2. Topological parameters at the bond critical points \mathbf{r}_b . First row: experiment. Second row: theory, B3LYP6-311++g(3df,3pd).

Compound	Bond	Lengths [Å]	d_1 [Å] ^[a]	$\rho(\mathbf{r}_b)$ [e Å ⁻³]	$-\rho(\mathbf{r}_b)$ [e Å ⁻⁵]	ϵ ^[b]
monofluoroethene	F–C1	1.347	0.88	1.78	0.5	0.05
	C1–C2	1.317	0.66	2.47	–29.0	0.41
1,1-difluoroethene	F11–C11	1.321(1)	0.788	2.16(3)	–20.9(3)	0.08
		1.321	0.88	1.95	–3.0	0.16
	F12–C11	1.320(1)	0.788	2.17(6)	–21.1(3)	0.08
		1.321	0.88	1.95	–3.0	0.16
	C11=C12	1.310(1)	0.737	2.55(5)	–25.8(3)	0.26
		1.315	0.75	2.43	–27.67	0.49
	F21–C21	1.321(1)	0.787	2.16(3)	–20.7(3)	0.09
		1.321	0.788	1.95	–3.0	0.16
	F22–C21	1.313(1)	0.790	2.19(6)	–22.3(3)	0.08
		1.321	0.788	1.95	–3.0	0.16
C21=C22	1.308(1)	0.736	2.56(5)	–26.0(3)	0.26	
	1.315	0.75	2.43	–27.67	0.49	
<i>(E)</i> -difluoroethene	F1–C1	1.344(1)	0.788	1.85(3)	–13.2(2)	0.09
		1.343	0.88	1.79	0.1	0.01
	C1=C1'	1.312(1)	0.656	2.47(3)	–29.3(3)	0.25
		1.319	0.66	2.48	–28.6	0.56
<i>(Z)</i> -difluoroethene	F1–C1	1.346(1)	0.764	2.11(3)	–20.3(3)	0.07
		1.338	0.88	1.82	0.33	0.01
	C1=C1'	1.315(1)	0.658	2.69(4)	–30.1(4)	0.49
		1.321	0.66	2.48	–28.4	0.56
trifluoroethene	F1–C1	1.317(1)	0.752	2.16(6)	–9.6(4)	0.05
		1.320	0.88	1.96	–2.3	0.22
	F2–C1	1.311(2)	0.753	2.19(9)	–11.2(4)	0.04
		1.314	0.88	1.98	–1.8	0.21
	F3–C2	1.345(2)	0.751	2.04(8)	–11.2(5)	0.10
		1.340	0.88	1.81	1.1	0.09
	C2=C1	1.309(2)	0.681	2.39(9)	–25.0(8)	0.69
		1.321	0.71	2.45	–28.1	0.68
tetrafluoroethene	F1–C	1.317(1)	0.801	2.16(3)	–16.6(2)	0.38
		1.317	0.88	1.97	–1.8	0.28
	F2–C	1.315(1)	0.832	2.10(4)	–23.7(3)	0.24
		1.317	0.88	1.97	–1.8	0.28
	C=C'	1.313(1)	0.659	2.41(8)	–29.5(1)	0.67
		1.321	0.66	2.47	–28.9	0.86

[a] d_1 is the distance from the first atom in the bond column to the bond critical point. [b] The ellipticity (ϵ) is $(\lambda_1/\lambda_2)-1$, where λ_1 and λ_2 are the two negative curvatures of $\rho(\mathbf{r})$ at \mathbf{r}_b .

fluoroethene^[45] (b.p. -42°C) and *(Z)*-1,2-difluoroethene^[44] (b.p. -20°C) were separated by distillation. The purities of the compounds were checked by IR and ^{19}F NMR spectroscopy, indicating isomeric purities of $>95\%$ for the *E* and $>90\%$ for the *Z* isomer. 1,1-Difluoroethene and trifluoroethene are commercially available and were used as received.

Crystal structure determinations: As the compounds are gaseous at ambient temperature, they were condensed into glass capillaries of 0.5 mm diameter and 0.01 mm wall thickness by use of a glass vacuum line. A column of 3–4 mm of the liquid was cooled with liquid nitrogen, and the capillary was sealed under vacuum at a length of 30 mm. After warming to -78°C in a dry ice acetone bath, the capillary was mounted on an insulated arcless goniometer head, while the sample was maintained at -78°C to avoid destruction of the capillaries.

The samples were mounted in the cold nitrogen gas stream of an integrated cooling device^[47] in a computer controlled Siemens four-circle single-crystal diffractometer with an Nb filter and $\text{MoK}\alpha$ radiation ($\lambda =$

0.7107 Å) (tetrafluoroethene, trifluoroethene, and 1,1-difluoroethene) or a Bruker-AXS SMART1000 diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.7107$ Å) (*(E)*-1,2-difluoroethene, *(Z)*-1,2-difluoroethene).

Different strategies were used for growing single crystals. On the Siemens diffractometer, single crystals were grown by setting the temperature of the gas stream to a few degrees below the melting point of each compound: -145 , -81 , and -148°C , respectively (m.p. = -142.5°C for $\text{F}_2\text{C}=\text{CF}_2$, m.p. = -78°C for $\text{F}_2\text{C}=\text{CFH}$, and m.p. = -144°C for $\text{F}_2\text{C}=\text{CH}_2$). The major part of the sample column was melted from its lower side by use of a coaxial coil of heating wire. With the aid of an electronic control device for the heat output of the coil, the phase border face was very slowly moved in the opposite, downward direction. Finally the crystal was annealed at the preset temperature.

On the Smart 1000 diffractometer, crystals of *(E)*-1,2-difluoroethene and *(Z)*-1,2-difluoroethene were grown by cooling of the samples well below

their melting points, slow warming to determine the melting points, and recoiling to obtain a polycrystalline material. Setting of the temperature of the cold nitrogen gas stream as close as possible (1 K) below the melting point resulted in a temperature gradient between the upper and lower part of the capillary, since the nitrogen gas stream is not parallel to the capillary axis because of the fixed χ angle of the diffractometer. Slow ϕ rotation resulted in single crystals after a few hours. The quality of the crystals and the progress of crystallization were checked by recording rotational frames and matrix runs. The crystals were cooled slowly to the temperatures given in Table 3. The structure solution was obtained by direct methods (SHELXS-97).^[48] Hydrogen atoms were located in the difference Fourier maps and refined isotropically by full-matrix, least-squares refinement based on F^2 (SHELXL-97)^[48] with anisotropic thermal displacement parameters in the spherical refinement for carbon and fluorine. Crystallographic data, measurement and refinement results are summarized in Table 3. Selected bond lengths and angles are summarized in Figure 1.

The crystals grown under low-temperature conditions in capillaries on the diffractometer were of sufficient quality to diffract to relative high resolutions [$(\sin \theta/\lambda)_{\max} = 0.95\text{--}1.14 \text{ \AA}^{-1}$], so charge density determinations based on Hansen–Coppens formalism^[49] could be performed by use of the XD program.^[50] The refinements, minimizing the quantity $\sum_{\mathbf{H}} w_{\mathbf{H}} (|F_{\text{o}}(\mathbf{H})| - k|F_{\text{c}}(\mathbf{H})|)^2$ with the statistical weight $w_{\mathbf{H}} = [\sigma(F_{\text{o}}(\mathbf{H}))]^{-2}$, were also carried out with the XD program.^[50] Only those structure factors meeting the criterion $F_{\text{o}}(\mathbf{H}) > 3\sigma(F_{\text{c}}(\mathbf{H}))$ were included. The multipole model was expanded up to the hexadecapole level ($L=4$) for the heavy atoms (C, F) and up to the dipolar level ($L=1$) for the hydrogen atoms. For the C and F atoms the individual radial screening parameters (κ) were assigned and refined. For the hydrogen atoms κ was fixed to 1.20. Because no neutron data were available the C–H distances were fixed to 1.08 Å as suggested by theory. As atomic site symmetry, a cylindrical symmetry was applied for the fluorine atoms and no symmetry for the carbon and hydrogen atoms. A model in which the cylindrical symmetry of fluorine atoms was left out was also considered. The statistical figures showed that the use of this symmetry fits the data as well as no local symmetry for fluorine atoms. As one example, the experimentally determined residual map of (Z)-1,2-difluoroethene is shown in Figure 9, which, except for a small signal close to the fluorine atom sites, is practically featureless.

CCDC-232281 (tetrafluoroethene), CCDC-232282 (trifluoroethene), CCDC-232280 (1,1-difluoroethene), CCDC-232279 ((Z)-1,2-difluoroethene) and CCDC-232283 ((E)-1,2-difluoroethene) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Table 3. Crystal, measurement, and refinement data.

	1,1-Difluoroethene	(E)-1,2-Difluoroethene	(Z)-1,2-Difluoroethene	Trifluoroethene	Tetrafluoroethene
formula	C ₂ F ₂ H ₂	C ₂ F ₂ H ₂	C ₂ F ₂ H ₂	C ₂ F ₃ H ₂	C ₂ F ₄
M_r [g mol ⁻¹]	64.04	64.04	64.04	82.03	100.02
T [K]	100	120	120	100	100
crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$Pnma$	$P2_1/n$	$P2_1/n$
a [Å]	5.3032(8)	4.929(2)	6.3938(8)	4.560(4)	4.551(2)
b [Å]	6.312(1)	4.452(2)	9.516(1)	14.386(2)	6.210(2)
c [Å]	16.989(3)	6.346(3)	4.4920(6)	4.7598(9)	5.775(2)
β [°]		106.32(1)		106.73(8)	104.35(7)
V [Å ³]/ Z	568.7(3)	133.7(1)	273.31(6)	299.0(4)	158.12(12)
Z	8	2	4	4	2
ρ [g cm ⁻³]	1.496	1.592	1.556	1.822	2.10
μ [mm ⁻¹]	0.18	0.19	0.19	0.24	0.29
$[(\sin \theta)/\lambda]_{\max}$ [Å ⁻¹]	0.95	1.14	1.06	1.01	1.08
reflns collected	7991	5255	7388	3996	3410
independent reflns	3789	1563	1168	2546	1682
R (int)	0.020	0.038	0.028	0.027	0.020
$R(F)$ spherical/multipole	0.035/0.032	0.045/0.035	0.041/0.030	0.05/0.041	0.031/0.024
$Rw(F)$ multipole	0.019	0.039	0.020	0.030	0.022

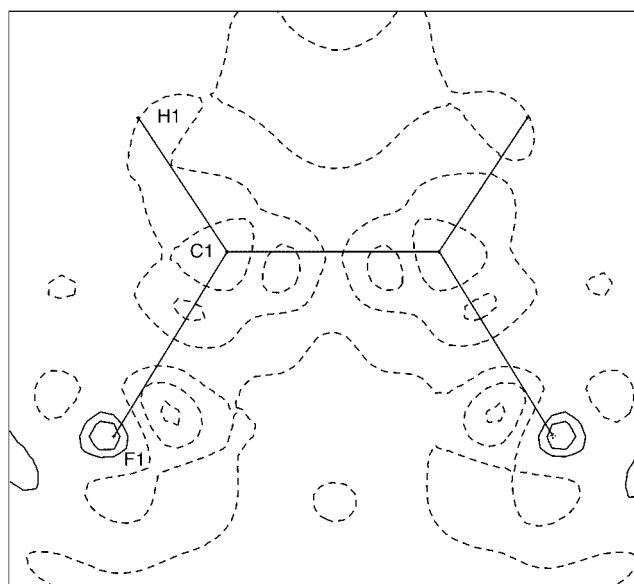


Figure 9. The residual map for (Z)-1,2-difluoroethene, with contour intervals of 0.05 e \AA^{-3} . Dashed lines represent negative and solid lines positive levels.

According to Bader's theory of atoms in molecules (AIM),^[51,52] a topological analysis of $\rho(\mathbf{r})$, which provides a quantitative description of charge density data, was applied. For comparison, a theoretical topological analysis was also carried out for the isolated molecules by use of the AIM-PAC program,^[53] based on B3LYP density functional ab initio calculations with the 6-311++G(3df,3pd) basis set.^[54]

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